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Modified Electrodes for Electrochemical Reduction of Carbon Dioxide

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Abstract

The efforts to constrain greenhouse gas emissions and concerns over security of fossil fuels have led to increased attention for renewable energy for the past decade. Renewable energy is one of the key solutions to the actual energy challenges. Omnidea in collaboration with Research Institutes is developing a technology based upon a regenerative energy storage cycle that could be a contribution to a low-carbon energy future. In this cycle the recharge system, which is composed of an electrochemical cell, converts CO_2 into fuel (hydrocarbons and hydrogen) using an external source of power (e.g. solar power).
The discharge system produces electric energy when hydrocarbons and oxygen from the recharge system are directly supplied to a Solid Oxide Fuel Cell (SOFC). Currently state of the art systems for direct electrochemical reduction of CO_2 exhibit low current densities and or low Faradaic efficiencies. Thus considerable research activity is still needed to develop electrodes with a performance suitable for an industrial application. This paper describes the progress to date and the work carried out with the aim of achieving this goal. It addresses particularly the modification of electrodes for electrochemical conversion of CO_2 and reports voltammetric studies as a tool for screening and optimizing electrodes for CO_2 conversion.

Keywords: *Energy, Carbon Dioxide, SOFC, Copper, Nickel*

1 Introduction

The conversion of carbon dioxide into hydrocarbons is a process that has been around since the early 1900s. The Sabatier process involves the conversion of CO_2 and hydrogen into methane and water in the presence of a nickel catalyst at high temperatures and high pressures:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (1)$$

Other approaches for using CO_2 to synthesize a fuel have been considered previously [1], but better CO_2 reduction processes are still lacking and further research in this field is needed. Such a process should use available inexpensive raw materials, have few process stages, be easily scalable and operate at room temperature. One-step electrochemical CO_2 reduction at a metallic electrode yielding a mixture of one- or two-carbon atom hydrocarbons and hydrogen

potentially fulfills these requirements. The basic raw materials for this process are CO_2 and water. Electrochemical reduction of CO_2 to yield fuel requires that hydrogen be present at some step of this reaction. Water can be used simultaneously as electrolyte and as an *in situ* source of hydrogen.

The aim of this ongoing research project is thus to develop a regenerative energy storage cycle.

In this cycle the recharge system, which is composed of an electrochemical cell, converts CO_2 into compounds (hydrocarbons) using an external source of power (e.g. solar power), Fig. 1. The discharge system produces electric energy when hydrocarbons and oxygen from the recharge system are directly supplied to a Solid Oxide Fuel Cell (SOFC).

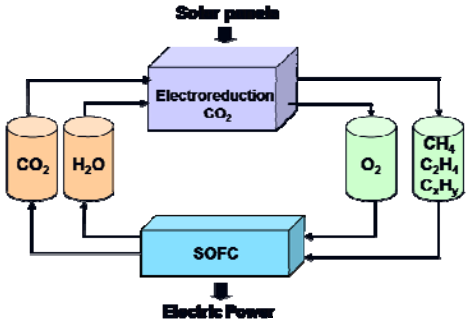

Figure 1. Regenerative energy storage cycle

2 Current Status of Present Research

Omnidea in collaboration with research institutes developed new electrodes based upon the modification of copper electrodes for the electrochemical reduction of CO_2 to hydrocarbon fuels (CH_4, C_2H_4 and C_2H_6) [2]. The initial results performed in a laboratory reactor, Figure 1, demonstrate that the electrolytic reduction of an aqueous solution of 0.1 M $KHCO_3$ using copper electrodes modified by electrodeposits yields a mixture of C_2 hydrocarbons, methane, CO and H_2. The presence of the electrodeposits changes the catalytic behaviour of the substrates resulting in a mixture of hydrocarbons with a higher energetic density per volume compared with the fuel resulting from CO_2 reduction without electrodeposits.

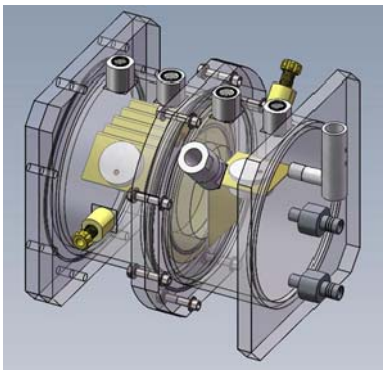

Figure 1. Cylindrical-shaped reactor with two compartments for electrolyte (1.5 l each)

By controlling the characteristics of the electrodeposits, mainly the surface area, ethylene (C_2H_4) and ethane (C_2H_6) can be selectively produced without any methane (CH_4) yielding fuels with a higher volumetric energy density (6.67 kWh/l for ethane as opposed to 3.38 kWh/l for methane).

Ongoing work addresses further optimization of these electrodes in particular to obtain sustained prolonged performance and in order to prepare/facilitate a scale up of the system [3]. To achieve this goal modification of an electrode of one metal with particles of another metal is under study. The introduction of low hydrogen-overpotential metal sites such as nickel, or ruthenium on a high hydrogen-overpotential metal surface e. g. copper, or vice versa allows catalytic interaction between both hydrogen and CO_2 adsorbed on the neighbouring sites. This interaction may result in a reduction of the overpotential and an improvement of selectivity for the CO_2 reduction.

Encouraging results were obtained [4] with modest nominal size electrodes. Based upon preliminary work Faradaic efficiencies for ethylene production are expected to be higher than 60%.

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